

the furnace through the ammeter and resistance shown at *a* in fig. 3. The coarse adjustment of the current is made by means of a water-cooled brass tube resistance. The current flows in series through two brass tubes 5 feet long fixed in a frame side by side, whilst a stream of water flows through to cool them. By means of two stout brass clips across the two bars any fraction of them can be short-circuited. The maximum resistance of these tubes is  $1/300$  ohm.

This furnace has been used in an investigation of the dissociation of cuprous oxide, and has been found to be in every way satisfactory.

Part of the expense of the construction of this furnace was defrayed by a grant from the Government Grant Committee of the Royal Society, to whom the author wishes to express his thanks.

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*An Investigation of the Dissociation Pressures and Melting Points  
of the System Copper-Cuprous Oxide.*

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E. Heyn\* determined the melting points of mixtures of copper and cuprous oxide of compositions varying between 100 per cent. Cu and 88.24 per cent. Cu, 11.76 per cent.  $\text{Cu}_2\text{O}$ . The results of his experiments are shown by the points marked + in fig. 1. These points fall on two curves intersecting at the eutectic point  $1065^\circ \text{C}$ .,  $\text{Cu}_2\text{O}$  3.5 per cent., Cu 96.5 per cent. Heyn found that all his mixtures showed a halt in the cooling curve at this eutectic temperature, so that within the range of his experiments there is no evidence of the existence of solid solutions.

C. N. Otin† has lately published some experiments on the melting points of the system cuprous oxide-silica. He attempted to determine the melting point of cuprous oxide, but as some oxidation always took place in his experiments, and as he did not analyse the solid obtained (on account of

\* 'Zeit. anorg. Chem.,' vol. 39, p. 11.

† 'Metallurgie,' vol. 9, p. 92.

having to remelt it to get it out of the platinum crucible), there is some doubt as to the actual composition of the substance of which he determined the melting point. The highest temperature at which he found a halt in the cooling curve was  $1205^{\circ}\text{C}$ .

Foote and Smith\* found that the dissociation pressure of cuprous oxide does not exceed 1 mm. at  $1020^{\circ}\text{C}$ .

It was the original intention of the authors to place a weighed amount of cuprous oxide in the furnace described in the previous paper, evacuate, heat to a certain temperature, determine the steady pressure obtained, and then to pump off the oxygen a little at a time, measure it, and determine again the steady pressure obtained. From the amount of oxygen pumped off the composition of the mixture of copper and cuprous oxide in the furnace at any time could have been determined after allowing for the known volume of the apparatus. In this way a series of pressure-composition isotherms would have been obtained, from which the pressure, temperature, and temperature-composition diagrams could have been constructed. This method was found to be impossible, owing to the rapid volatilisation of the mixture from the boat into the cool ends of the tube, and it became necessary to investigate that portion of the melting point diagram which was untouched by Heyn, in order to explain the results of our dissociation pressure measurements.

*The Melting Point Diagram.*—Two samples of cuprous oxide obtained from Kahlbaum were analysed by reduction in hydrogen and were found to contain 14.5 and 8 per cent. CuO respectively. The former was a sample which had been in the laboratory stock for three years.

The cuprous oxide used in the following experiments was made by reducing an alkaline solution of copper sulphate with grape sugar at  $60^{\circ}\text{C}$ . in presence of tartaric acid. The product usually contained a small quantity of metallic copper.

The copper used in making up the mixtures for melting point determinations was either powder reduced from the oxide by heating in hydrogen, or electrolytic copper in the form of short pieces of thin wire.

The oxide or mixture of oxide and metal was placed in an unglazed crucible of Royal Berlin porcelain of the form generally sold as a Rose crucible. These crucibles were found to be quite inappreciably attacked by  $\text{Cu}_2\text{O}$  or CuO, even when exposed to their action for an hour at  $1350^{\circ}\text{C}$ . Each crucible held about 25 gm. of the mixture. The thermo-couple was protected by tubes of the same material as the crucibles. The thermo-couple was threaded through one of the tubes intended for introducing the

\* 'Amer. Chem. Soc. Journ.,' vol. 30, p. 1344.

gas into a Rose crucible, so that the junction was about the middle of the tube. By heating at this point in an oxy-gas flame the tube softened and could then be bent double at the point which contained the junction.

The crucibles were heated in a platinum-wound resistance furnace, through which was passed a stream of  $\text{CO}_2$  to avoid oxidation of the charge. After the substance had become completely melted, the heating current was cut off and the cooling curve obtained. The temperatures were read on a millivolt meter which was checked from time to time by means of a potentiometer. The couple was of platinum-platinum-rhodium; it had been calibrated at the melting point of copper.

After the cooling curve had been obtained the mass was broken up, separated from the adhering pieces of crucible, and analysed by reduction in hydrogen. Over a certain range of composition it was found that two layers were formed. The lower one rich in copper and the upper one rich in cuprous oxide, the following results were obtained:—

Table I.

| No. of layers.      | Composition.                                            | Melting point. |
|---------------------|---------------------------------------------------------|----------------|
| 1 .....             | 98.6 per cent. $\text{Cu}_2\text{O}$ , 1.4 per cent. Cu | 1203°          |
| 2 (top layer) ..... | 96.1 " $\text{Cu}_2\text{O}$ , 3.9 " Cu                 | 1195°          |
| (bottom layer) ...  | Too small to analyse.                                   |                |

Some experiments were then made in which the melt was heated to a known steady temperature for 30 to 60 minutes and then the crucible rapidly removed from the furnace and quenched in water. In one experiment the crucible was allowed to cool very slowly in the furnace so that equilibrium might be attained at the lowest temperature at which the two phases could exist, that is at 1195°.

Table II.

| Temperature of quenching.    | Bottom layer.           |           | Top layer.              |           |
|------------------------------|-------------------------|-----------|-------------------------|-----------|
|                              | $\text{Cu}_2\text{O}$ . | Cu.       | $\text{Cu}_2\text{O}$ . | Cu.       |
|                              | per cent.               | per cent. | per cent.               | per cent. |
| 1340° .....                  | 22.15                   | 77.85     | 93.16                   | 6.84      |
| 1254° .....                  | 21.0                    | 79.0      | 92.1                    | 7.9       |
| (1195°, cooled slowly) ..... | 20.2                    | 79.8      | 94.54                   | 5.46      |

In the two following experiments mixtures of copper and cuprous oxide were melted in a carbon tube resistance furnace and quenched from temperatures in the neighbourhood of  $1400^{\circ}\text{C}$ . Two layers were formed in each case, having the following compositions:—

Table III.

| Experiment. | Bottom layer.           |                    | Top layer.              |                   |
|-------------|-------------------------|--------------------|-------------------------|-------------------|
|             | $\text{Cu}_2\text{O}$ . | Cu.                | $\text{Cu}_2\text{O}$ . | Cu.               |
| E .....     | per cent.<br>21·98      | per cent.<br>78·02 | per cent.<br>90·87      | per cent.<br>9·13 |
| F .....     | 23·07                   | 76·93              | 91·94                   | 8·06              |

These results are shown graphically in fig. 1. The results of Heyn are marked, +, those of Table I,  $\odot$ , those of Table II,  $\oplus$ , and those of Table III,  $\times$ .

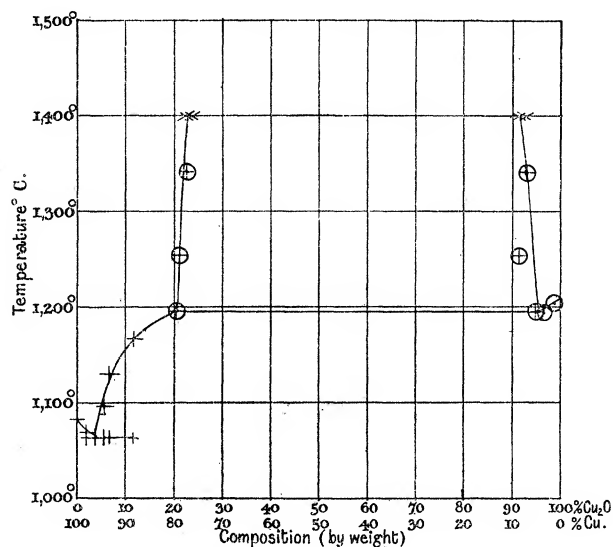


FIG. 1.

The figure shows that the system is similar to that of phenol and water. The melting point of pure cuprous oxide is about  $1210^{\circ}\text{C}$ . At temperatures above  $1195^{\circ}$  mixtures having a composition between 20 per cent. and 95 per cent. cuprous oxide separate into two layers. The above results show that up to  $1400^{\circ}\text{C}$  there is only a slight narrowing of this range of concentration, that is to say increase of temperature only slightly increases the solubility of

one liquid phase in the other. It is, however, just possible that the quenching was not rapid enough and that in all the experiments the equilibrium obtained was approximately that at  $1195^{\circ}$ .

*Dissociation Pressures.*—From the melting point diagram we can, by means of the phase rule, determine what type of  $p, t$  (pressure, temperature) diagram will be obtained. Since the system contains two components, copper and oxygen, there must be three phases present for one degree of freedom, or in the usual notation of the phase rule  $F = n + 2 - P = 4 - P$ . That is to say, if there are three phases present there will be a definite pressure corresponding to each temperature, but if there are only two phases present—*e.g.* liquid and gas—the pressure will depend on the composition as well as upon the temperature. The  $p, t$  diagram (projection on the  $p, t$  surface) will be of the type shown in fig. 2.

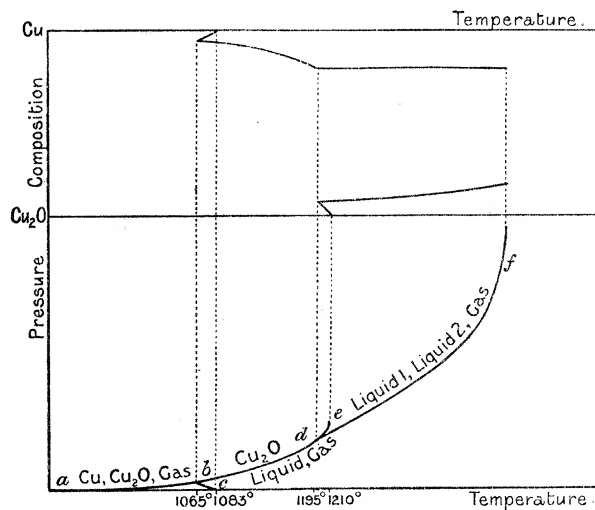


FIG. 2.

The lines represent the pressures of the following mono-variant systems :—

- $ab$ , system solid Cu, solid  $\text{Cu}_2\text{O}$ , gas.
- $bc$ , „ solid Cu, liquid, gas.
- $bde$ , „ solid  $\text{Cu}_2\text{O}$ , liquid, gas.
- $df$ , „ liquid (1), liquid (2), gas.

The point  $b$  represents the non-variant system solid Cu, solid  $\text{Cu}_2\text{O}$ , liquid, gas; the point  $d$  the system solid  $\text{Cu}_2\text{O}$ , liquid (1), liquid (2), gas.

It was found that below  $1200^{\circ}$  the pressure of the system was so small and equilibrium was attained so slowly that it was impracticable to determine any points on  $ab$ ,  $cb$ , or  $bd$ . Nor were any points on  $de$  obtained owing to the short range both of temperature and composition of this line.

*Apparatus.*—The furnace described by one of us in the preceding paper (p. 519) was used. The tube *i* was sealed to a tube which could be dipped in liquid air and which led to the vacuum gauge and Töpler pump. The arrangement is shown in fig. 3.

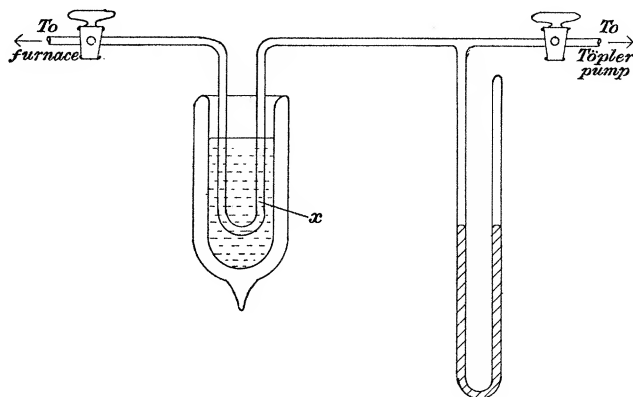


FIG. 3.

During all the experiments the portion *x* of the tube was kept immersed in liquid air to condense any  $\text{SO}_2$  and  $\text{CO}_2$  evolved from the magnesia boat and so prevent them from affecting the measurements of the oxygen pressure. Behind the vacuum gauge was a glass millimetre scale illuminated by a lamp and milk-glass screen. The readings were made with a telescope; they were accurate to 0.1–0.2 mm.

The magnesia boats used at first were made as follows: Pure magnesia was fused in an electric arc or resistance furnace, ground up until it passed through a sieve with 90 meshes to the inch, and then made into a paste with magnesium chloride solution. A carbon mould having been made for the boat, it was lined with the paste and then dried, first at  $30^\circ$ , then at  $150^\circ$ . The boat had now become quite hard owing to the formation of magnesium oxychloride and adhered firmly to the mould. Mould and boat were then gradually heated in a granular carbon resistance furnace up to  $1800\text{--}2000^\circ\text{C}$ . On opening the furnace the boat was quite hard and had become loose from the mould.\* These boats were quite refractory, but were unsuitable for the work in hand because the liquid mixtures of Cu and  $\text{Cu}_2\text{O}$  were rapidly absorbed by the porous magnesia. Besides this it was found that these boats gave off large quantities of  $\text{SO}_2$ . This obviously comes from the sulphur absorbed by the magnesia from the retort carbon in which it was baked. One of these boats having a volume of about 4 c.c. of magnesia on heating *in vacuo* to  $1400^\circ\text{C}$ . gave off 35 c.c. of  $\text{SO}_2$ .

\* *Vide* Slade, 'Chem. Soc. Journ.,' vol. 93, p. 327.

These two defects were overcome by making the boats in the following way: A vertical carbon electrode made an arc with the bottom of a carbon crucible; magnesia was then fed into the crucible to smother the arc.\* In three or four minutes, when the magnesia had been well melted by the high power arc of 30–40 kw., the current was cut off. A piece of solid magnesia, like an irregularly-shaped teacup glazed on the inside, was found in the crucible. In such a lump one or two portions suitable for a boat, when cut away from the mass, would be found. The lump was carefully broken to preserve these portions, and the boats finally shaped by grinding on an emery wheel. These boats were taken from the lump in such a way that the inside of the boat was formed of the glazed surface of the magnesia round the arc.

After the tube had been in use for some time and a deposit of  $\text{Cu}_2\text{O}$  had formed on the cool parts, a run was made with the furnace empty. The pressure rose only to 0.4 mm. in one hour at  $1380^\circ\text{C}$ .

The cuprous oxide was prepared as described in the first part of this paper. In most of the experiments a small quantity of electrolytic copper was added to the cuprous oxide, so that if the cuprous oxide had been slightly oxidised we should, after heating up, have the system  $\text{Cu}_2\text{O}-\text{Cu}$  and not the system  $\text{CuO}-\text{Cu}_2\text{O}$ . The boats held about 0.4 grm. of cuprous oxide.

*Experiment.*—The results of experiments on the dissociation pressure are shown in fig. 4, where the pressures are plotted as ordinates against the time as abscissæ. Each continuous curve is an isotherm. The temperature, during an experiment lasting up to eight hours, was usually kept within  $1^\circ\text{C}$ . and always within a range of  $4^\circ$ .

Curves I, II, III, and IV are dissociation curves of the system liquid (1)–liquid (2)–gas. It is seen that after about three hours the pressure becomes quite steady, when the temperature is  $1200$ – $1260^\circ$ , but a much shorter period is necessary for equilibrium to be attained at  $1324^\circ$  (Curve III). Curve V is the dissociation curve of the di-variant system liquid–gas at  $1240^\circ$ . In this case, where there was not sufficient copper present to form two liquid phases, the pressure was still rising after five hours; no equilibrium was reached. The explanation of this is obviously that Cu was being volatilised more rapidly than  $\text{Cu}_2\text{O}$  from the liquid phase, which thus became richer in  $\text{Cu}_2\text{O}$ , and so had a higher oxygen pressure. From analogy with other metals we should expect the metal to have a greater vapour pressure than the oxide. In those experiments in which there were two liquid phases present volatilisation would only affect the quantity of the two

\* Both the eyes and face of the operator must, of course, be suitably protected from the ultra-violet light of such an arc.

liquid phases and not their composition; therefore so long as neither of the liquid phases had completely disappeared the system had a definite oxygen pressure.

The quantity of copper and cuprous oxide left in the boat after an experiment was, in only one case, enough for an analysis of sufficient accuracy to determine whether there had been one or two liquid phases present during the experiment. Usually more than half of the mixture had been volatilised from the boat. An analysis of the boat at the conclusion of one experiment (Curve II) gave Cu 0.1956 grm., O<sub>2</sub> 0.0216 grm. This corresponds

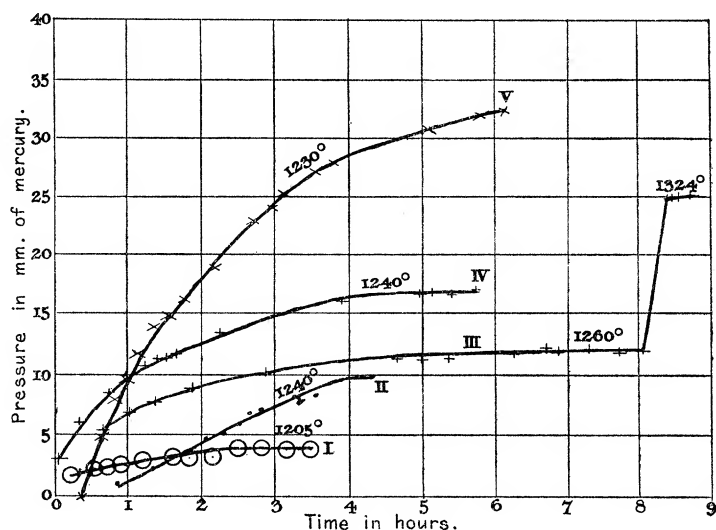


FIG. 4.

to a mixture containing 11.05 per cent. Cu, 88.95 per cent. Cu<sub>2</sub>O. Such a mixture would form two liquid phases at the temperature of the experiment, 1240°, as may be seen by reference to fig. 1.

The vapour pressure of copper at these temperatures may be calculated with a fair degree of accuracy as follows:—Greenwood\* has determined the boiling point of copper at one atmosphere to be 2310° C., and has shown that the effect of pressure on the boiling point of copper is similar to its effect on mercury. Thus

$$T_1/T_2 = t_1/t_2,$$

where  $T_1$  and  $t_1$  are the absolute boiling points of copper and mercury respectively at one atmosphere pressure, and  $T_2$  and  $t_2$  their boiling points at some other pressure. Let this latter pressure be that exerted by copper

\* 'Zeit. Phys. Chem.,' vol. 76, p. 487.

at  $1300^{\circ}\text{C}$ ., that is  $1573^{\circ}$  absolute. Then the temperature on the absolute scale at which mercury would have this same pressure is

$$t_2 = \frac{t_1 \times T_2}{T_1} = \frac{630 \times 1573}{2583} = 388.$$

The pressure of mercury at this temperature— $115^{\circ}\text{C}$ .—is approximately 1 mm. This is, therefore, also the vapour pressure of copper at  $1300^{\circ}\text{C}$ .

It might be expected that the  $\text{Cu}_2\text{O}$  would not be appreciably volatile *per se*, but that it would only volatilise by dissociating into copper and oxygen which, when they have diffused into the cooler parts of the apparatus, recombine, but this does not seem to be the case, for the authors find that a small piece of  $\text{Cu}_2\text{O}$  can be volatilised from a platinum strip at  $1300^{\circ}\text{C}$ . in a few minutes, even in air where the oxygen pressure is too great for dissociation into copper and oxygen to take place, and would cause partial oxidation to cupric oxide.

Curve IV shows the results of an experiment in which a small piece of platinum was added to the mixture of cuprous oxide and copper to determine whether it would raise the dissociation pressure. This was found to be the case, a steady pressure of 16 mm. being obtained, whilst at the same temperature— $1240^{\circ}\text{C}$ .—without the platinum the dissociation pressure was 10 mm. This experiment was undertaken to explain an earlier experiment, in which an abnormally high pressure had been obtained, and where it was found that a little of the oxide had been upset on to the hot part of the platinum tube.

The four values obtained for the pressure of the system liquid (1)—liquid (2)—gas are given in Table IV and plotted in fig. 5. This is a portion of the curve *df* of fig. 2.

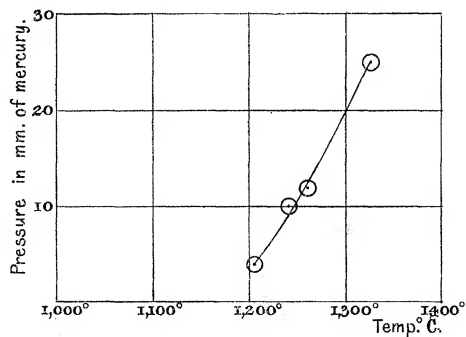


FIG. 5.

Table IV.

| Temperature in °C. | Pressure in mm. of Hg. | No. of curve in fig. 4. |
|--------------------|------------------------|-------------------------|
| 1205               | 4                      | I                       |
| 1240               | 10                     | II                      |
| 1260               | 12                     | III                     |
| 1324               | 25                     | III                     |

In one experiment at 1230° the system liquid-gas gave a pressure of 39 mm. after five and a-half hours, but the pressure was still steadily rising, owing to volatilisation of copper from the liquid phase, making the latter continually richer in cuprous oxide.

*Thermodynamic Theory.*—Allmand\* has calculated the dissociation pressure of the system solid  $\text{Cu}_2\text{O}$ -solid Cu-gas at 17° C. from measurements of the E.M.F. of the cell  $\text{Cu}/\text{Cu}_2\text{O}.\text{NaOH}/\text{Pt}.\text{H}_2$  and found  $3 \times 10^{-53}$  atmosphere. He has also calculated this pressure by means of the Nernst formula, which in this case is

$$\log p = -Q/4.57 T + 1.75 \log T + C,$$

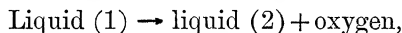
where  $Q = 81,600$  and  $C = 2.8$ .

If  $T = 290$  (17° C.),  $p = 3 \times 10^{-55}$  atmosphere.

Using this same formula Stahl† has calculated that at 1662° C.  $p = 0.21$  atmosphere.

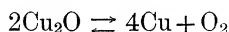
For 1250° C., about which our experiments were made, we get  $p = 0.45 \times 10^{-3}$  atmosphere = 0.34 mm.

This is the pressure we should expect for the system solid  $\text{Cu}_2\text{O}$ -solid Cu-gas at 1250° C., if it could exist at this temperature, and assuming that the heat of reaction did not vary with the temperature. For the system liquid (1)-liquid (2)-gas at 1250° C. we get from our experimental results 11 mm. There are no data available for applying Nernst's formula to this equilibrium, for we should require to know the heat of the reaction



where liquid (1) is the phase rich in cuprous oxide and liquid (2) that rich in copper.

Allmand (*loc. cit.*) points out that the law of mass action applied to the equilibrium



gives the equation

$$K = (P_{\text{Cu}}^4 \times P_{\text{O}_2}) / P_{\text{Cu}_2\text{O}}^2,$$

\* 'Chem. Soc. Journ.', vol. 95, p. 2163.

† 'Metallurgie,' vol. 4, p. 682.

so that at a given temperature we should expect  $P_{O_2}$  greater, if in place of the solid system we had the system solid  $Cu_2O$ -liquid-gas since  $P_{Cu}$  would be lower for liquid than for solid,\* and the pressure of the liquid copper would be lowered by the formation of the solution. In the system of which we have measured the pressure, liquid (1)-liquid (2)-gas, both  $P_{Cu}$  and  $P_{Cu_2O}$  will be lower than they would be if both the metal and oxide remained solid up to the temperature under consideration. Since, however,  $P_{O_2}$  is proportional to  $P_{Cu_2O}^2$ , and inversely proportional to  $P_{Cu}^4$ , if the ratio in which  $P_{Cu}$  and  $P_{Cu_2O}$  are lowered is the same in both cases, the relative lowering of the value of  $P_{Cu}^4$  would be much greater than that of the value of  $P_{Cu_2O}^2$ ; we should therefore expect  $P_{O_2}$  to be greater for the liquid than for the solid systems. As is shown above, the experimental value for the liquid systems is greater than that calculated on the assumption that the system is solid at that temperature.

If the heat of dissociation  $q$  does not vary with the temperature, we may apply the formula of van't Hoff

$$q = -4.584 (\log p_2 - \log p_1) \frac{T_1 T_2}{T_2 - T_1},$$

to calculate  $q$  from our measurements at two temperatures. We find from the values at  $1205^\circ$  and  $1260^\circ$  C.

$$q = -90,060 \text{ cal.},$$

and from the values at  $1260^\circ$  and  $1324^\circ$

$$q = -55,890 \text{ cal.}$$

At ordinary temperature, the value of  $q$  for the dissociation of solid  $Cu_2O$  into solid copper and oxygen is  $-81,600$  cal.

From the two values calculated from our experiments it is obvious that  $q$  is not independent of the temperature, and this is what we should expect if the composition of the two liquid phases changed with the temperature. In our experiments we found a small change of composition with temperature, though, as is pointed out on p. 528, this effect may be somewhat greater than is indicated in fig. 1.

The authors' best thanks are due to Prof. F. G. Donnan for his kind interest and encouragement during the course of this investigation, and to Mr. R. Kingan for assistance in the analyses. Part of the expenses of this research were met by a grant from the Government Grant Committee of the Royal Society, to whom the authors wish to express their thanks.

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\* That is to say, the pressure curve for liquid lies below that of superheated solid.